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ELECTRICAL CONDUCTIVITY OF SOLUTIONS IN AMYL AMINE

BY

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A Thesis Submitted for the Degree of MASTER OF SCIENCE

UNIVERSITY OF WISCONSIN
1903

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ELECTRICAL CONDUCTIVITY OF SOLUTIONS IN AMYL AMINE

A considerable amount of work has been done in investigating the electric conductivity of solutions, both aqueous and non-aqueous. From the behavior of the former class of solutions the conclusion has been drawn that the greater the dilution, the greater the degree of dissociation of the molecules, hence the greater the electrical conductivity. But upon the study of the behavior of non-aqueous solutions, which have been found to digress from this theory of electrolytic dissociation upon increase of dilution. a question has been raised as to the validity of the assumption which the Hence it would seem that some amendtheory presupposes. ment, at least, should be added to the affirmation at present made in regard to the electrical conductivity of solutions, since the exceptions are too numerous to pass unnoticed.

Previous investigation made along this line in this laboratory, suggested that further work might be done to advantage. The work above referred to was done by 0. E. Ruhoff upon solutions of silver nitrate, cadmium iodide and ferric

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chloride in amyl amine. In accordance with the idea of determining the behavior of various other salts in amyl amine, the results given below were obtained.

The method used for taking the measurements was that of Kalrausch. The method of dilution and the form of cell used were the same as those employed by Ruhoff. 2

Particular pains were taken to have the amyl amine and the salts free from moisture.

The specific conductivity of $\frac{N}{50}$ potassium chloride solution was taken as 0.00277 reciprocal ohms at 25 degrees Centigrade. The results in any case are not corrected for the conductivity of the solvent. The last measurement in each case of the amyl amine solutions, is that of the saturated solution. A few preliminary quantitative measurements were made of the conductivity of some aqueous solutions which had already been determined as sodium chloride and copper sulphate. The specific conductivity of the water used was 7.71 x 10^{-6} reciprocal ohms. The resistance capacity of the cell or the constant, K, was 0.24108. The measurements were made at 25 degrees Centigrade.

The abbreviations used throughout the paper indicate the

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¹⁰stwald: Physico-chemical measurements.
20. E. Ruhoff: B. S. Thesis, - The Electrical Conductivity of Solutions in Amyl Amine.

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following: t the temperature, k the resistance capacity of the cell, sp. c. the specific conductivity, \underline{v} the volume, in cubic centimeters, of the solution containing one gram molecule of the salt; $\underline{\mathbb{X}}_{\mathbf{v}}$ the molecular conductivity.

COPPE	COPPER SULPHATE		SODIUM CHLORIDE			
Sp. C.	v.	Mv	Sp. C.	v.	M _v	
.000203	647,589	131.4	.00077	163,284	126.1	
.000426	310,303	132.2	.00382	30,337	115.8	
.000766	144,607	110.8	.00466	24,564	114.5	
.000895	118,210	105.8	.00568	19,756	112.2	
.001124	86,596	97.3	.00786	13,982	109.9	
.001872	46,113	86.3				
.002840	26,837	76.2				
.003804	18,479	70.3				
.004660	14,377	6 6. 9				
.006523	9,262	60.4				
.008349	6,739	56.3				
.01174	4,648	54.6				
.016947	2,734	46.3				
.019493	2,265	44.2				

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The number of salts used was necessarily limited, and they showed a considerable variation in their solubility and conductivity in amyl amine.

The following salts were found to be apparently insoluble; nitrate and chloride of barium; chloride and nitrate of calcium; zinc iodide, strontium nitrate, nitrate and acetate of lead, platinum chloride, nitrite and sulphate of silver. The copper salts were all soluble. The sulphate and chloride dissolved readily, giving decidedly blue solutions. The cyanide dissolved very easily, giving a deep blue solution. The aceto acetic ester was sparingly soluble, giving a greenish blue solution.

The acetate and carbonate did not go into solution in as great a degree as the other copper salts and gave paler blue solutions. Mercuric chloride and bromide were readily soluble, the bromide exceeding the chloride considerably in solubility. The tri-chloride of antimony formed a precipitate and was apparently insoluble. Potassium sulpho-cyanide went into solution with difficulty. Lead chromate was only slightly soluble. Cadmium nitrate showed slight solubility. Ferrous chloride dissolved. Chloride of cobalt went into solution easily. Mercurous chloride turned black and appeared to be insoluble. Strychnine zinc iedide gave a white precipitate and was insoluble.

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silver acetate dissolved easily and seemed to decompose at once giving a black solution. Cadmium acetate was soluble. Silver tartrate was fairly soluble, giving a brown solution containing more or less sediment. Silver palmitate also gave a brown solution with a sediment. Of the three silver salts used in making the quantitative measurements the solubilities ranged approximately in the ratio of 4:35:1, the silver iodide being most soluble, the silver chloride being least soluble, the silver bromide coming in between.

There seemed to be no constant relation between solubility and conductivity, as some of the salts which dissolved
most readily and gave highly colored solutions, showed no conduction, while other salts, only sparingly soluble gave solutions of fair conduction.

In order to determine the conductivity of the solutions qualitatively they were placed in circuit with a battery in the following manner. A small platinum crucible was used to which was fitted a hard rubber cover. This cover was perforated and a copper wire passed through it, which was soldered to a platinum wire, which, in turn, was soldered with gold to a small platinum disc. The platinum wire was of such length that the disc came within about one millimeter of the bottom of the crucible. The crucible acted as one electrode while the disc acted as the other.

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Enough solution was placed in the crucible to cover the disc and the circuit closed. If there was sufficient conduction to be measured, a sensitive galvanometer, placed in the circuit, indicated the passing of a current by a swing of the needle. The angle of perfection was read in degrees on the scale.

The solutions of the copper salts gave no qualitative results for conductivity. The silver acetate solution gave a reading of thirteen degrees. It was dried and tried for quantitative results, but as the resistance was found to be so high that it could not be accurately measured the above reading was probably due to moisture present in the salt when measured qualitatively. The cadmium acetate solution gave no deflection of the galvanometer needle. The silver tartrate solution gave a reading of about one-quarter of a de-The salt being dry a quantitative measurement was gree. tried but the conduction was not sufficient to give a reading. The silver palmitate solution gave a reading of about onequarter of a degree. It was dried and tried for quantitative Indefinite minimums were obtained on the bridge indicating some conduction, but further investigation found this to be due to sediment which settled out on the bottom of the cell, short circuiting the electrodes. The silver nitrite solution, while the salt was apparently insoluble, gave

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a deflection of five-tenths of a degree. A quantitative measurement was attempted and indefinite minimums were obtained but were found to be due to the same cause as in the case of the silver palmitate solution. The silver sulphate solution gave no galvanometer reading. The potassium sulphocyanide solution gave a galvanometer reading of eight degrees. The nitrate of cadmium gave the same results as the potassium sulphocyanide solution. The ferrous chloride solution gave a very slight deflection, only a small fraction of a degree. The solution of chloride of cobalt gave a reading of five degrees. No quantitative determinations were made with these four salts on account of the difficulty of drying them satisfactorily.

Careful quantitative measurements were made of solutions of the following salts in amyl amine; mercuric bromide, mercuric chloride, copper sulphate, silver iodide, silver bromide, silver chloride and silver cyanide.

The mercuric bromide solution gave a reading of eleven degrees on the galvanometer. When the salt was put in the smyl amine it looked somewhat waxy and stuck to the glass, but dissolved quite readily. The solution remained clear up to about the dilution of one gram molecule in 995.3 cc., when it became opalescent. After the dilution of one gram molecule in 826.7 cc. the salt dissolved very slowly and the solu-

• • • • · . • • • . • ment settled on the bottom of the cell. The minimum was not clear for any of the measurements, there being a range of at least ten centimeters. Through an inadvertence the observations were made at twenty-four and six-tenths degrees Centigrade instead of at twenty-five degrees Centigrade. The same was also true for the mercuric chloride.

Specific conductivity of the amyl amine was 1.45 x 10. $^{-6}$ K = .24108.

The mercuric chloride solution gave a reading on the galvanometer of five-tenths of a degree. The quantitative measurements showed a high resistance, so high that the results obtained were not very satisfactory. The solution became opalescent and a white sediment settled out when allowed to stand.

Specific conductivity of the amyl amine was 1.45 x 10. $^{-6}$ K = .24087. 1

Regardless of the fact that the copper sulphate solution gave negative qualitative results, a quantitative measurement was taken. The amount of salt used was small, being but 0.0255 gram. Some of it went into solution, giving a blue

'Tabulated results are given on page 9.

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MERCURIC BROMIDE.

MERCURIC CHLORIDE.

v.	M ^A	Sp. C.	٧.	M
3518	.00243	7.03 x 10	11982	.0084
3369	.00229	1.81 x 10	_ ⁶ 3090	.0056
3094	.00303	4.04 x 10	- ⁶ 2160	.0087
2895	.00298			
2559	.00717			
2169	.01009			•
2052	.01609			
1836	.02130	COPPE	R SULPHA!	re.
1639	.03278		••	
1405	.05915	Sp. C.	γ.	M _v
995.3	.1602	7.05 x 10	11982	.0084
973.3	.1781	/. 5 × / 6 - 5	46228	8.32 X/0
879.6	.2076			
826.7	.2249			
765.5	.2342			
	3518 3369 3094 2895 2559 2169 2052 1836 1639 1405 995.3 973.3 879.6 826.7	3518 .00243 3369 .00229 3094 .00303 2895 .00298 2559 .00717 2169 .01009 2052 .01609 1836 .02130 1639 .03278	3518 .00243 7.03 x 10 3369 .00229 1.81 x 10 3094 .00303 4.04 x 10 2895 .00298 2559 .00717 2169 .01009 2052 .01609 1836 .02130 COPPE 1639 .03278 1405 .05915 995.3 .1602 7.05 x 10 973.3 .1781 879.6 .2076 826.7 .2249	3518 .00243 7.03 x 10 -7 11982 3369 .00229 1.81 x 10 5090 3094 .00305 4.04 x 10 -6 2160 2895 .00298 2559 .00717 2169 .01009 2052 .01609 1836 .02130 COPPER SULPHAN 1639 .03278 1405 .05915 995.3 .1602 7.05 x 10 11982 973.3 .1781 879.6 .2076 826.7 .2249

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color to the amyl amine. There was found a flocculent precipitate which increased the resistance in the same manner as reducing the size of the plates.

Specific conductivity of the amyl amine was 1.7 \times 10. $^{-7}$ K = .2051.

Temperature, 25° Centigrade.1

The halogen salts of silver, silver iodide, silver bromide, and silver chloride were prepared and used for the following measurements. The salts were carefully dried and
protected from the light. The solutions of these salts gave
no deflection on the galvanometer, the apparatus not being
sufficiently sensitive to record the conductivity.

The silver bromide was readily soluble and as a result of the decomposition of the salt, after the second measurement the solution began to get dark and continued to do so until it became a dark brown color. There was no definite minimum before the last six dilutions, there being a range of at least ten centimeters on the bridge. For some reason, the first three measurements decrease after which there is a steady increase. The decrease in the next to the last dilution is doubtless due to an experimental error.

In taking the observations for the last dilution, the

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^{&#}x27;Tabulated results are given on page 9.

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solution had stood over night and as it was saturated, the salt had crystallized out, forming a mass of crystals in the bottom of the cell. In the liquid, which had the consistency of a syrup, were floating very delicate crystals of tabular shape. A black sediment was also present. In order to get a measurement of the saturated solution, the cell was placed in water at a temperature of about thirty degrees Centigrade. When the crystals were dissolved the cell was introduced into the water bath at twenty-five degrees Centigrade and a measurement attempted; but as the salt crystallized out rapidly upon the solution cooling down to the required temperature, a satisfactory result was not obtained.

Specific conductivity of the amyl amine was 1.7 x $10.^{-7}$ K = .2051.

Temperature, 25° Centigrade.

The silver chloride was not so soluble as the silver bromide. The solution became somewhat dark, caused by the presence of a sediment held in suspension, which would settle out
on standing. The salt crystallized out in a mass for the
last measurement. The crystals were scale-like in shape.
An experimental error of some kind introduced an irregularity
for the dilution of a gram molecule in 1300 cubic centimeters.

^{&#}x27;Tabulated results are given on page 12.

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SILVER BROWIDE..

SILVER CHLORIDE.

S	p. C.	₹,.	N.	Sp. C.	Y	M _v
7.09	x 10 ⁻⁷	5662	.00401	1.89 x 10 ⁷	5135	.00097
4.96	x 10 ⁷	3192	.00158	4.49×10^{-7}	3105	.00139
5.23	x 10 ⁻⁷	2111	.00110	6.29×10^{-7}	2350	.00148
9.08	x 10 ⁻⁷	1463	.00133	9.35 x 10 ⁻⁷	1917	.00160
8 .67	x 10 ⁻⁷	1256	.00109	10.7 x 10 ⁻⁷	1300	.00139
1.26	x 10 ⁻⁶	1075	.00135	13.35 x 10 ⁷	1232	.00164
L .9 8	x 10 ^e	928	.00184	16.53 x 10 ⁷	1146	.00189
2.89	x 10-6	778	.00225	20.2 x 10 ⁷	1004	.00203
9.14	x 10 e	678	.00620	36.9 x 10 ⁷	923	.00340
3.09	x 10 ⁻⁵	576	.01204	45.2 x 10 ⁷	864	.00391
1.55	x 10 ⁻⁶	487	.02216			
7.05	x 10 ⁻⁵	464	.03271			
72	x 10°	432	.04199	SILVE	R IODID	E.
1.47	x 10 ⁴	393	.05777	G= C	V	v
5.07	x 10 ⁻⁴	329	.10100	Sp. C.	٧.	м^А
3.13	x 10 ⁻⁴	305	.09547	1.558 x 10	⁷ 38 8	.0000605
5 .6 5	x 10 ⁻⁴	279	.10184			

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Specific conductivity of the amyl amine was less than

K = .2428.

Temperature = 25° Centigrade.

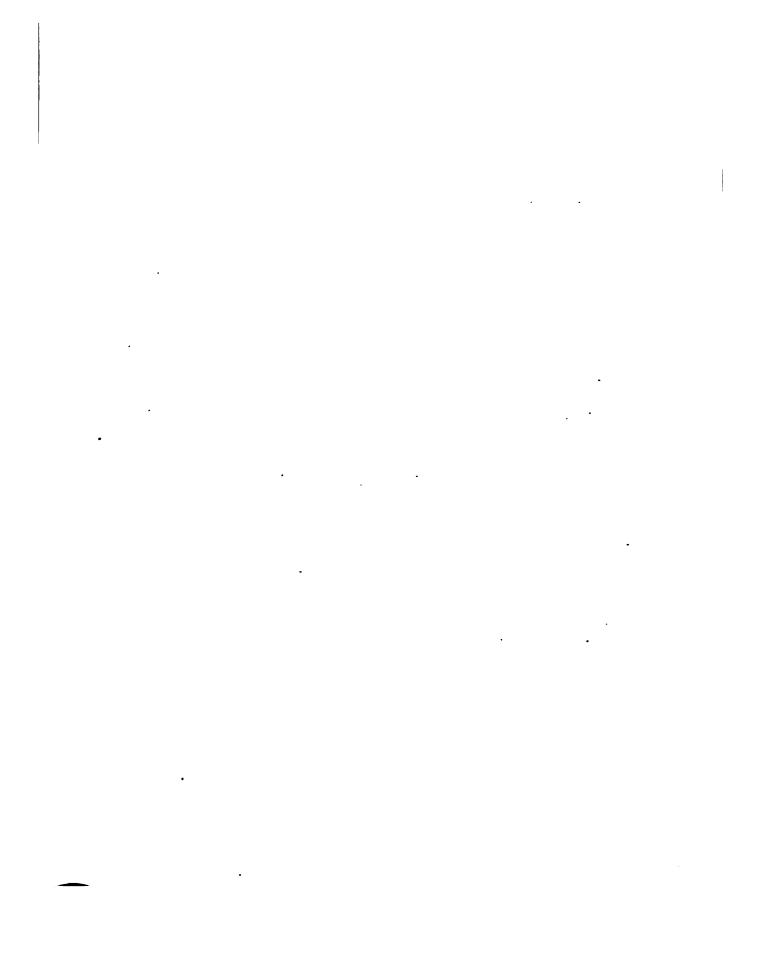
The silver iodide solution did not show sufficient conduction to be measured by the apparatus used, so the cell was set up in circuit with a galvanometer and a high E. M. F. applied. It was found that it took 110 volts to give a reading of two and five-tenths degrees on the galvanometer. The galvanometer was then calibrated by using an ammeter and one degree was found to equal .000028 ampere. From these data the resistance of the cell was calculated to be 1,571,428 ohms. But one measurement was taken for the molecular conductivity with the results given below.

Specific conductivity of the amyl amine was less than .294 x 10^{-7}

Temperature = 25° Centigrade.1

Silver cyanide was quite soluble and showed good conduction after the third reading, before which there was a range of from thirty to twenty centimeters on the bridge. The solution became black from the sediment held in suspension,

Tabulated results are given on page 12. Tabulated results are given on page 15.



which settled out upon standing for some time. When the solution was saturated, a mass of flake like crystals separated out leaving a thin, clear solution.

Specific conductivity of the amyl amine was 4.5×10^{-7} Temperature = 25° Centigrade.

The molecular conductivity of mercuric bromide shows some irregularity in the first four results due in all probability to experimental errors, since the following figures show a steady increase in conductivity. The molecular conductivity of the mercuric chloride decreased and then increased upon further concentration of the solution. But one measurement was made of the molecular conductivity of the copper sulphate so no comparison can be made.

The molecular conductivity of the silver bromide shows for the first three measurements a decrease of conductivity upon concentration of the solution. There is then a slight increase when it again goes down, but after this last irregularity the conductivity steadily increases with the concentration with the exception of the next to the last result, where some slight experimental error was introduced in some way. The molecular conductivity of the silver chloride shows an increase in conductivity up to the fifth measurement, where it drops down considerably, after this irregularity it in-

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SILVER CYANIDE.

SI	o. c.	٧.	N A	Sp.	c.	V.	u
1.36	x 10 ⁻⁶	25808	.0351	.956	x 10-	1243	1.1883
.253	x 10-5	14664	.0375	1.34	x 10-8	969	1.2985
.334	x 10 ⁻⁸	10233	.0342	1.68	x 10-3	800	1.344
1.87	x 10 ⁻⁸	5979	.1118	1.96	x 10 ⁻³	678	1.33
.690	x 10-4	3846	.2654	2.13	x 10-3	596	1.2695
1.91	x 10-4	2699	.5155	2.35	x 10 ⁻³	483	1.1351
.250	x 10-3	2263	.5658	2.4	x 10-8	422	1.0128
.528	x 10 ⁻³	1749	.9235	2.35	x 10 ⁻³	337	.7919
.806	x 10-3	1384	1.1155				

creases with the concentration. But one result was obtained for the molecular conductivity of the silver iodide, so no comparison of results can be made. The molecular conductivity of the silver cyanide drops down considerable in the third result, doubtless due to an experimental error, after which it increases with the concentration up to the thirteenth result, with which it begins to decrease and the decrease continues through the remainder of the measurements.

It is seen from the data previously given that the conductivity of salts in amyl amine is very slight. The resist-

• • • . ance is high and extremely sensitive apparatus would be required in order to obtain more satisfactory results.

In conclusion it may be said that the conductivity of a non-aqueous solution is apparently not dependent upon the number of dissociated molecules since the molecular conductivity increased, in all cases, with the concentration.

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